Selective Membrane Separations for Ammonia

W.A. Phillip, E. Martano, L. Chen, Marc A. Hillmyer and E.L. Cussler
Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

Membranes made of crosslinked block copolymers of styrene and sulfonated styrene are over one hundred times more permeable to ammonia than to nitrogen and hydrogen. This selectivity, measured with mixed gases, is the same as that expected from the fluxes of pure gases, i.e., the actual selectivity is within experimental error the same as the ideal selectivity. The membranes may find application in separating the outlet stream of the Haber process reactor.

Background. The basis for the "Green Revolution" in food production is still ammonia produced by the 1909 Haber process. In this process, nitrogen and hydrogen react over a ruthenium-promoted iron catalyst at 180 bar and 400°C. The high temperature, necessary for rapid kinetics, restricts the conversion to around 20 percent. As a result, the product gases are typically cooled to 10°C to condense the ammonia and allow nitrogen and hydrogen to be recycled. Significant amounts of nitrogen and hydrogen also dissolve in the liquid ammonia complicating further processing.

As a result, many have suggested separating the ammonia from the mixed product gases using a membrane. Several membranes show promise, including cellulose acetate[1,2], polyvinyl-ammonium thiocyante[3,4], and polyperfluorosulfonates (e.g., Nafion[5]. These membranes operate by a diffusion-solubility mechanism known to exist for ammonia for over one hundred years. Such membranes do show much higher permeabilities for ammonia than for other gases;

that is, they have an ideal selectivity of over one thousand. However, when these membranes are fed with mixed gases, the actual selectivity is modest, less than ten.

In this work we extend knowledge gained in this earlier work to make a new membrane based on polystyrene-co-styrene sulfonate.[6] Crosslinked films of this membrane retain the ideal selectivity when fed with mixed gases.

Results. The experiments in this work are based on membranes 50-150 μm thick mounted in the diaphragm cell shown in Figure 1(a). This cell consists of two compartments separated by a membrane. The top, "donating" compartment initially contains gases at high pressure. The

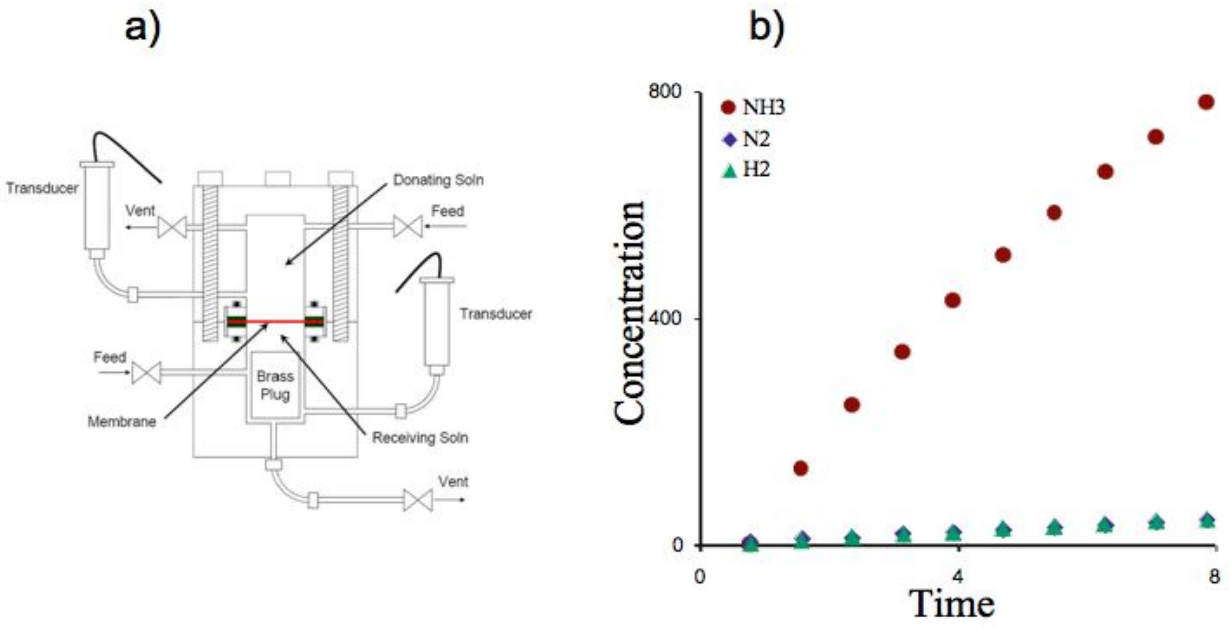

Figure 1. Results with Pure Gases. The experiments use the diaphragm cells shown in (a). In this cell, the pressure in the receiving solution, which is initially zero, is measured *vs.* time. For a Nafion membrane shown in (b), the ammonia pressure rises more than one hundred times faster than that of hydrogen or nitrogen.

contents of the bottom, “receiving” compartment depend on the particular experiment. For experiments with one gas, the bottom compartment contains all but one of the gases in the top compartment. In these mixed-gas experiments, all but one of the gases are at the same partial pressures on both sides of the membrane. Experiments with one gas are exemplified by the results for 130 μm Nafion membranes in Figure 1(b). The data show that ammonia is much more permeable than the other gases. Indeed, the ideal selectivity is over 1000:1.

The results for mixed gases, shown in Figure 2, give a more complex and more interesting result. For Nafion, the promise of the pure gas experiments in Figure 1(b) is lost, as shown by the data in Figure 2(a). In this figure, the mixed gas data show a selectivity of about

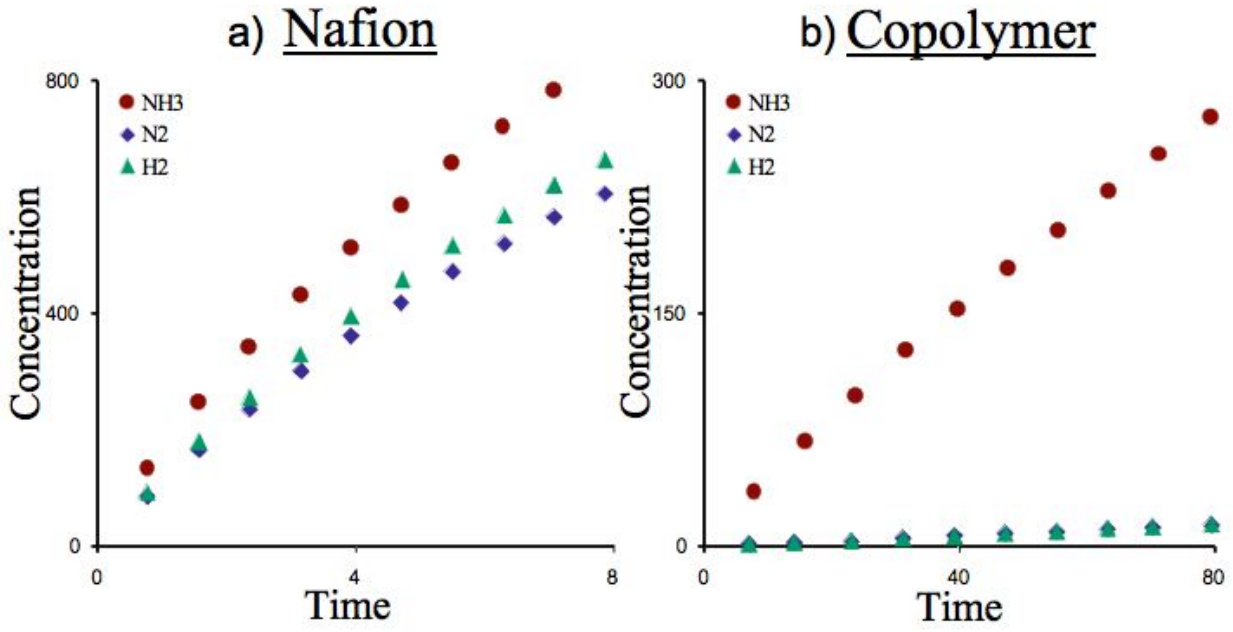

Figure 2. Results with Mixed Gases. Nafion membranes, shown in (a), show almost no selectivity when fed with mixed gases. Block copolymer membranes, shown in (b) retain a selectivity of over 100.

2:1, a shadow of the ideal selectivity of 1000:1. In sharp contrast, for the block copolymer, the selectivity for ammonia in mixed gases remains over 100, as shown in Figure 2(b). The block copolymer membrane is successful.

We are not sure why this is so. We recognize that the promise of ideal selectivity is often not realized and that this disappointment is especially well studied for carbon dioxide-methane separations.[7-9] We originally thought that because the block copolymer membranes are tightly crosslinked, they would swell less in ammonia than Nafion does, but we cannot measure any difference. We can see no major changes in the SAXS patterns for the two systems. However, while we do not definitively know why the block copolymer membrane works, it does. It keeps its ideal selectivity and works well.

REFERENCES

1. Bickson, B., Nelson, J.K., and Perrin, J.E., U.S. Patent 5,009,678, April 23, 1991.

2. Vorotyntsev, I.V., Drozdov, P. N., Karyakin, N. V., Ammonia permeability of a cellulose acetate membrane. *Inorganic Materials* **42**(3) (2006) 231-235.

3 Laciak, D.V., and Pez, G.P., U.S. Patent 4,758,250, July 19, 1988; Pez, G.P., and Laciak, D.V., U.S. Patent 4,762,535, August 9, 1988.

4. Bhown, A., Cussler, E.L., Mechanism for selective ammonia transport through poly(vinylammonium thiocyanate) membranes, *J. Am. Chem. Soc.* **113** (1991) 742.

5. He, Y., Cussler, E.L., Ammonia permeabilities of perfluorosulfonic membranes in various ionic forms, *J. Memb Sci* **68** (1992) 43.

6. Chen. L, Phillip, W.A., Cussler, E.L. Hillmyer, M.A., Robust nanoporous membranes templated by a doubly reactive block copolymer, *J. Am. Chem. Soc.* **129** (2007) 13786.

7. Staudt-Bickel, C., and Koros, W.J., "Improvement of CO_2/CH_4 Separation Characteristics of Polyimides by Chemical Crosslinking," *J. Memb. Sci.* **155** (1991) 145-154; cf. also U.S. patent 7,169,885, January 30, 2007.

8. Visser, T., Masetto, N., Wessling, M., Materials dependence of mixed gas plasticization behavior in asymmetric membranes, *J. Memb. Sci.* **306**(1+2) (2007) 16-28.

9. Zhao, H., Cao, Y. Ding, X., Zhou, M. Yuan, Q., Poly(N,N-dimethylaminoethyl methacrylate)-poly(ethylene oxide) copolymer membranes for selective separation of CO_2, *J. Memb Sci* **310** (2008) 365.